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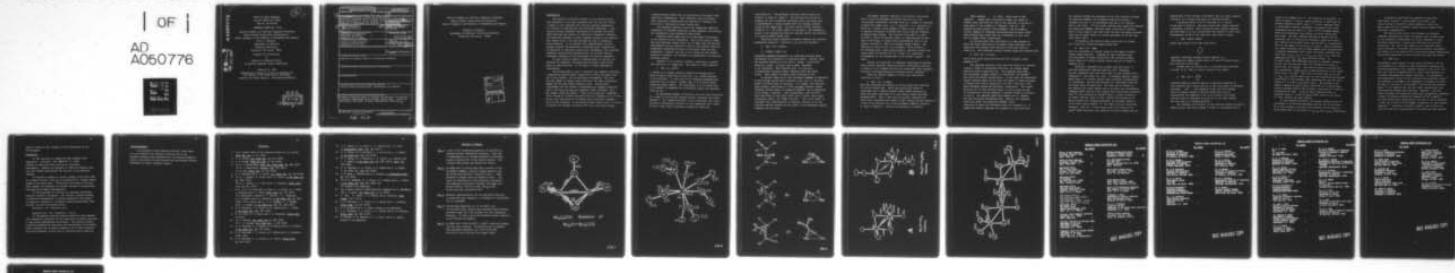
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Recent Findings in the Chemistry of Molybdenum and Tungsten
by M. H. Chisholm

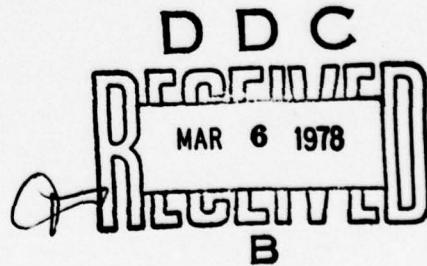
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Reaction Schemes for Dinuclear Compounds Containing
Metal-to-Metal Triple Bonds Illustrated by
Recent Findings in the Chemistry of Molybdenum and Tungsten

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Introduction

The ability of transition metals to form multiple bonds with themselves is now well recognized and over the past decade a number of such compounds have received detailed examination by a variety of spectroscopic and structural techniques.¹ More recently certain compounds containing M-M quadruple and triple bonds have been the subject of theoretical treatments.² However, the reactivity patterns of these compounds remains to be explored. This should prove a rich and exciting new area of transition metal chemistry. It is possible that organometallic reaction schemes evolved³ for mononuclear transition metal complexes may be applicable to dinuclear systems and, furthermore, that dinuclear compounds could provide building blocks for the much desired systematic syntheses of new polynuclear and cluster compounds.⁴

In this account a number of general modes of reaction are proposed for compounds containing metal-to-metal triple bonds. These are then discussed in the light of recent experimental observations.

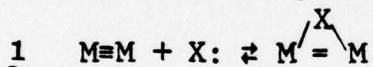
The notation M≡M is used to represent any compound containing a homonuclear metal-to-metal triple bond in which the metal atoms are in very similar, if not equivalent environments: they have the same number of valence shell electrons, the same coordination number and the same formal oxidation state. Fitting these requirements are two classes of molybdenum and tungsten compounds. Class I are M_2X_6 and $M_2X_{6-n}Y_n$ compounds, where Y=R(alkyl), NR₂, OR, O₂CNR₂, O₂COR and halide.⁵ Class II are Cp₂M₂(CO)₄ compounds (M=Cr, Mo and W) in which the metal atoms are formally in the +1 oxidation state and attain an 18-valence shell electronic configuration by the formation of the metal-to-metal triple bond.⁶ In class I the metals are formally trivalent (M^{3+}) and, even after forming

a metal-to-metal triple bond, do not attain an 18-valence shell electronic configuration. Both oxidation state and valence shell electronic configuration are expected to influence the reactivity of the metal-to-metal triple bond.

The proposed reactions involve the symmetrical addition/elimination of substrate molecules to M=M compounds: the products are considered to have equivalent metal atoms.

Reactions which might lead to an odd number of electrons in the products are not considered. This is not meant to imply that such reactions cannot occur, nor to imply that odd electron intermediates are not involved in some of the proposed reactions. [Compounds containing M-M bonds of fractional order are well documented?] However, thus far in our studies we have neither obtained as products, nor detected as intermediates, odd electron dinuclear species.

Addition of X: to M=M in reaction 1 represents a carbene-like addition to a triple bond. The moiety X: could indeed be

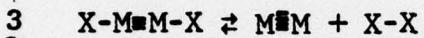
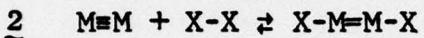


a carbene or an organic molecule capable of reacting with a metal-to-metal triple bond in this way, e.g., carbon monoxide or an isonitrile. X: could also be an inorganic/organometallic substrate such as $Fe(CO)_4$, Cp_2NbH , SnR_2 or a d^8 square planar transition metal complex. The requirement of X: is merely that it is capable of expanding its coordination number and oxidation state by two.

An interesting example of reaction 1 has just been discovered in a study of the reaction between $Mo_2(OR)_6$ compounds and carbon monoxide.⁸ The compound $Mo_2(OBu^t)_6$ reacts reversibly with carbon monoxide in hydrocarbon solvents at room temperature and 1 Atmos to give a deep purple crystalline compound $Mo_2(OBu^t)_6CO$,

$\nu(\text{CO})=1670 \text{ cm}^{-1}$. The molecular structure deduced from X-ray studies⁸ is shown in Figure 1. The molecule has virtual C_{2v} symmetry and the coordination polyhedron about each metal atom is approximately a square pyramid with the bridging carbonyl carbon at the common apex. The short metal-to-metal distance, 2.498(1) Å (c.f. Mo-to-Mo=2.222(1) Å in $\text{Mo}_2(\text{OR})_6$), the diamagnetic nature of the compound and electron counting require the existence of a metal-to-metal double bond.

Reactions 2 and 3 represent oxidative addition and reductive elimination sequences. Reactions 1, 2, and 3 all involve a



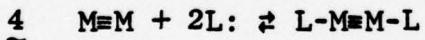
reversible addition/elimination of a substrate molecule which contributes two electrons to a dinuclear center. However, since the proposed reactions proceed with a change in M-M bond order, the number of metal valence shell electrons is not increased. This contrasts with the reactions of mononuclear transition metal complexes where the metals change their number of valence shell electrons by two.

At present there are no well documented examples of reactions 2 and 3 though several known compounds could serve as excellent models for these types of reactions. For example, the compounds $\text{M}_2\text{Me}_2(\text{O}_2\text{CNR}_2)_4$ when heated to $>150^\circ\text{C}$ in vacuo eliminate ethane yielding residues which, by elemental analyses, may be formulated as $\text{M}_2(\text{O}_2\text{CNR}_2)_4$ compounds. Both $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ and $\text{Mo}_2(\text{OPr}^1)_6$ have been found to react with acetic acid to yield, upon vacuum sublimation (200°C , 10^{-4} cmHg), $\text{Mo}_2(\text{OAc})_4$. Here a M-M triple to quadruple bond transformation is achieved, reaction 3, but the detailed reaction pathway and the nature of the eliminated organic compounds are not known.

The simple oxidative addition of X-X across a M-M triple bond to yield an unbridged M-M double bond has yet to be structurally established, although there are a number of reactions in which this might occur, e.g.,⁷ $\text{Cp}_2\text{M}_2(\text{CO})_4 + \text{I}_2 \rightarrow \text{Cp}_2\text{M}_2(\text{CO})_4\text{I}_2$. There are, however, known examples of where an X-X addition to a compound containing a multiple bond occurs with the formation of metal-ligand bridges. The reaction of $\text{Mo}_2(\text{OPr}^{\text{i}})_6$ to give $\text{Mo}_2(\text{OPr}^{\text{i}})_8$, which is discussed later, is representative of this type of M-M triple to double bond transformation since in the product, $\text{Mo}_2(\text{OPr}^{\text{i}})_8$, there are bridging alkoxy ligands. The addition of X_2 ($\text{X}=\text{I}$ or Br) to $\text{Mo}_2(\text{S}_2\text{COEt})_4$, which contains a M-M quadruple bond, yields $\text{Mo}_2\text{X}_2(\text{S}_2\text{COEt})_4$ compounds having Mo-Mo single bonds (Mo-to-Mo=2.72 Å) as a result of a surprising rearrangement in the bonding mode of the xanthate ligand.⁹ (See later).

Clearly the reactivity of compounds containing M-M multiple bonds towards oxidative addition/reductive elimination reactions is going to be as complex and even less predictable than analogous reactions involving mononuclear transition metal complexes.¹⁰

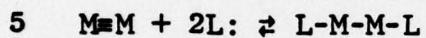
There are several examples of Lewis base association reactions of type 4.



Here four electrons are donated to the M_2 center with retention of the M-M triple bond. Lewis base association should be applicable only to metal-to-metal triple bonded compounds in which the metal atoms have 16 or less valence shell electronic configurations. This is the case for $\text{Mo}_2(\text{OR})_6$ compounds and these react reversibly with amines to give adducts $\text{Mo}_2(\text{OR})_6(\text{amine})_2$.¹¹ A view of the central core of the $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_6$ molecule is shown in Figure 2. The Mo-to-Mo distance is 2.242(1) Å.

Other examples in which metal atoms in M=M compounds expand their coordination number and number of valence shell electrons are seen in the reactions of $\text{Mo}_2(\text{OR})_6$,¹² $\text{W}_2\text{Me}_2(\text{NET}_2)_4$ ¹³ and $\text{W}_2(\text{NMe}_2)_6$ ¹³ compounds with CO_2 . The products $\text{Mo}_2(\text{OR})_4(\text{O}_2\text{COR})_2$, $\text{W}_2\text{Me}_2(\text{O}_2\text{CNET}_2)_4$ and $\text{W}_2(\text{O}_2\text{CNMe}_2)_6$ provide examples of compounds containing metal-to-metal triple bonds between metal atoms that are coordinated to four, five and six ligand atoms, respectively.

In contrast Lewis base association to a M=M compound in which the metal atoms have an 18-valence shell electronic configuration will proceed with reduction in M-M bond order as shown in 5. The reversible reaction between $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ ($\text{Mo}-\text{Mo}=2.40\text{\AA}$)

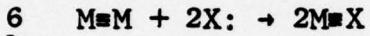


and CO which gives $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ ($\text{Mo}-\text{Mo}=3.27\text{\AA}$) provides a good example of 5.⁶

The compounds $\text{Cp}_2\text{M}_2(\text{CO})_4$ have also been found to be reactive towards a number of unsaturated molecules, un, giving simple addition products $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{un})$. The compounds where M=Mo and un= $\text{PhC}\equiv\text{CPh}$, $\text{EtC}\equiv\text{CEt}$, $\text{HC}\equiv\text{CH}$,^{14,15} $\text{CH}_2=\text{C}=\text{CH}_2$ ¹⁶ and Me_2NCN ¹⁷ have been structurally characterized. In all cases the unsaturated organic molecule spans the Mo₂ bond (see Figure 3) which increases in length from 2.40\AA in $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ to 2.974 , 3.015 and 3.117\AA where un= $\text{HC}\equiv\text{CH}$, Me_2NCN and $\text{CH}_2=\text{C}=\text{CH}_2$, respectively. The organic molecules act as four electron donors to the M₂ group and may be considered as further examples of products formed in reactions of type 5. The compound $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ (allene) has C_2 symmetry and thus equivalent molybdenum atoms. However, the compounds $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RC}_2\text{R})$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{NCNMe}_2)$ adopt structures in which the molybdenum atoms are inequivalent. In $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RC}\equiv\text{CR})$ compounds the asymmetry is associated with

the carbonyl bonding and presumably arises from internal crowding. In $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{NCNMe}_2)$ the bridging Me_2NCN group donates a nitrogen lone pair to one molybdenum atom and a CN π -electron pair to the other. ^{13}C nmr studies indicate that $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PhC}_2\text{Ph})$ and $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{NCNMe}_2)$ compounds adopt structures in solution akin to those found in the solid state and that low energy processes cause the two metal centers to become equivalent on the nmr time scale above -40°C .

In reaction 6 the metal-to-metal triple bond is cleaved and replaced by a metal-to-ligand triple bond.



There is, therefore, no overall change in the number of metal valence shell electrons. Although not many substrates meet the requirement of being carbyne-like, the reactions between nitric oxide and a metal-to-metal triple bond may be viewed as examples of 6.

$\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds react readily with NO(2 equiv) to give the mononuclear complexes $\text{CpMo}(\text{CO})_2(\text{NO})$.¹⁸ Similarly, $\text{Mo}_2(\text{OR})_6$ compounds react with NO(2 equiv) to give $[\text{Mo}(\text{OR})_3(\text{NO})]_2$ compounds.¹⁹ Here there are a pair of bridging alkoxide ligands, which leads to a fourteen valence shell electronic configuration for molybdenum. The Mo-to-Mo distance is 3.325 Å which precludes any direct metal-to-metal bond. The dimer may be cleaved by the addition of a donor ligand such as pyridine and a mononuclear compound $\text{W}(\text{OBu}^t)_3(\text{NO})(\text{py})$ has recently been structurally characterized.^{19b} The structure of $[\text{Mo}(\text{OPr}^i)_3\text{NO}]_2$ is shown in Figure 4. In $\text{W}(\text{OBu}^t)_3(\text{NO})(\text{py})$ there is also a linear M-N-O moiety in an axial position of a trigonal bipyramidal; the pyridine ligand is in the other axial position.^{19b} The value of the NO stretching frequency, 1555 cm^{-1} , is the lowest known for a linear M-N-O group²⁰ which indicates very extensive W-to- $\text{NO}\pi^*$ bonding and the

significance of the resonance form $M=N-\ddot{O}$: [The two other resonance structures for a linear M-NO group are $M=N=\ddot{O}$; and $M-N=\dot{O}$].

A potential source of an $X:$ substrate is, of course, an $X=X$ type of molecule. Reaction 6 would then simply represent a metathesis reaction. Since transition metal carbyne complexes are well known it is not inconceivable the reaction 7 could occur. Alternatively an $X=X$ or $2X:$ substrate could react to form a

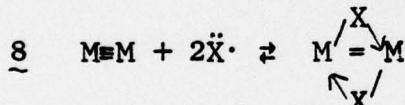


planar M_2X_2 moiety of the type shown below



Compounds containing bridging carbyne ligands, e.g., $[(Me_3SiCH_2)_2M(\mu-CSiMe_3)]_2$ where $M=Nb$, Ta^{21} and W^{22} , contain planar M_2C_2 moieties of this type.

Another mode of reaction for a 3 electron donor substrate is shown in 8. This is closely related to the simple



oxidative-addition reaction shown in 2 and may be expected to occur whenever the X moiety has one or more lone pairs of electrons, providing that the formation of the two $M-X-M$ bridges does not require rupture of the $M-M$ double bond as in 5. Alternatively the addition of $2X:$ or $X-X$ across a $M-M$ triple bond may occur as indicated in 2 and one of the other ligands may then take up a bridging position.

The formation of $Mo_2(OPr^i)_8$ in the reaction between $Mo_2(OPr^i)_6$, $AgPF_6$ (2 equiv) and proton sponge (2 equiv) in isopropanol may be

viewed as an example of 8.²³ The structure of $\text{Mo}_2(\text{OPr}^{\text{i}})_8$ is shown in Figure 4, where a simple comparison is made with the related compound $\text{Mo}_2(\text{OPr}^{\text{i}})_6(\text{NO})_2$.¹⁹ In both compounds there is essentially trigonal bipyramidal coordination about each molybdenum atom and there is a pair of $\text{Pr}^{\text{i}}\text{O}$ bridging ligands which form alternately long (axial) and short (equatorial) Mo-O bonds. The most striking differences between the two structures are (i) the Mo-to-Mo distances, which are 3.335(2) and 2.525(1) \AA for $\text{Mo}_2(\text{OPr}^{\text{i}})_6(\text{NO})_2$ and $\text{Mo}_2(\text{OPr}^{\text{i}})_8$, respectively, and (ii) the angles of the $\text{Mo}_2(\mu-\text{O})_2$ moiety. These differences are readily accounted for by simple ligand field considerations. A trigonal bipyramidal field splits the metal d orbitals into three sets e' ($d_{x^2-y^2}, d_{xy}$), e'' (d_{xz}, d_{yz}) and a' (d_{z^2}) with the degenerate pair d_{xz}, d_{yz} lying lowest in energy. In $\text{Mo}_2(\text{OPr}^{\text{i}})_6(\text{NO})_2$ each molybdenum atom may be assumed, formally, to have four 4d electrons after the formation of σ -bonds to each of the five ligands. This form of electron counting uses the conventional, though purely formal description of the linear Mo-N-O group as $\text{M}^- \text{--NO}^+$. These four electrons then occupy the e'' (d_{xz}, d_{yz}) orbitals where they can very effectively participate in Mo-to-No π^* back bonding, thus explaining the very low value (1632 cm^{-1}) of $\nu(\text{NO})$ in $\text{Mo}_2(\text{OPr}^{\text{i}})_6(\text{NO})_2$. The bonding in the dimeric compound $\text{Cr}_2(\text{OPr}^{\text{i}})_6(\text{NO})_2$ ($\nu(\text{NO})=1720 \text{ cm}^{-1}$) and the mono-nuclear compound $\text{W}(\text{OBu}^{\text{t}})_3(\text{NO})(\text{pyridine})$ ($\nu(\text{NO})=1555 \text{ cm}^{-1}$) must be essentially the same. In all of these compounds there is extensive metal e'' -to- $\text{NO}\pi^*$ bonding which, based on the values of $\nu(\text{NO})$, follows the order $\text{W}>\text{Mo}>\text{Cr}$.

In the compound $\text{Mo}_2(\text{OPr}^{\text{i}})_8$, the formal oxidation state of molybdenum is +4 and each molybdenum atom has two 4d electrons. It is thus possible to envision the formation of the metal-to-metal double bond as the result of $d_{xz}-d_{xz}$ and $d_{yz}-d_{yz}$ interactions.

It should be noted that the compounds $M_2(OR)_6(NO)_2$, $M(OR)_3(NO)L$, $Mo_2(OPr^i)_8$ and $Mo_2(OBu^t)_6CO$ provide a new class of Group VI transition metal complexes in which the metal atoms are five coordinate having fourteen valence shell electronic configurations.

The factors which lead to the formation of dinuclear compounds containing M-M bonds of multiple order n rather than to the formation of polynuclear or cluster compounds in which the metal atoms form n σ -bonds with each other are not well understood. The size of the ligands is one important factor and in principle a reversible association reaction, represented by 9 below, is to be expected for certain metal-ligand combinations. The possible geometries for the M_4 moiety are many and include



tetrahedral, square planar and open chain structures. We are not presently in a position to make predictions concerning the preferred geometries of M_4 compounds formed in 9 but we do note that this type of oligomerization is found in the chemistry of trivalent molybdenum and tungsten alkoxides. For molybdenum, the neopentoxide exists in both dinuclear and polynuclear forms.²⁴ The ethoxide is tetrameric and diamagnetic in benzene and shows $Mo_4(OEt)_{12}^+$, $Mo_3(OEt)_9^+$ and $Mo_2(OEt)_6^+$ ions in the mass spectrometer.²⁴ For tungsten only the very bulky triethylsiloxy and tertiarybutoxy ligands give dinuclear compounds. The less bulky isopropoxy and neopentoxy groups give tetranuclear complexes. A black crystalline tetranuclear compound $W_4(OPr^i)_{12}(HOPr^i)_2$, has been structurally characterized (see Fig. 5) and is believed to have one of the two Pr^iOH ligands coordinated at each terminal tungsten.²⁵ Formation of $W_4(OPr^i)_{12}(HOPr^i)_2$ may be viewed as the first step in a polymerization of $W_2(OPr^i)_6$ (an $M \equiv M$ compound)

which is halted in this instance by the coordination of the $\text{Pr}^{\text{i}}\text{OH}$ ligands.

Conclusions

(1) The reactions of symmetrical M=M compounds with symmetrical substrates are expected to yield products in which the metal atoms are in equivalent environments. Whenever an exception is found low energies pathways will readily interconvert the two ends of the dinuclear compound.

(2) Reactions leading to stepwise changes in M-M bond order are possible and may or may not be accompanied by a formal valence change of the metal atoms. Predictions with regard to M-M bond order changes are presently not possible because of uncertainties regarding metal-ligand rearrangements.

(3) The potential for carrying out dinuclear hydrocarbon catalysis should be recognized. One catalytic sequence leading to selective hydrogenation is already suggested by the ability of $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds to coordinate unsaturated molecules that are four- but not two-electron donors:



(4) The general reactions proposed herein for M=M compounds with symmetrical substrates are not exhaustive but merely pertinent to some recent experimental observations. The reaction schemes involving unsymmetrical substrates and heteronuclear M-M¹ multiple bonded compounds are virtually unlimited, all of which indicates the growth potential of this area of transition metal chemistry.

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Captions to Figures

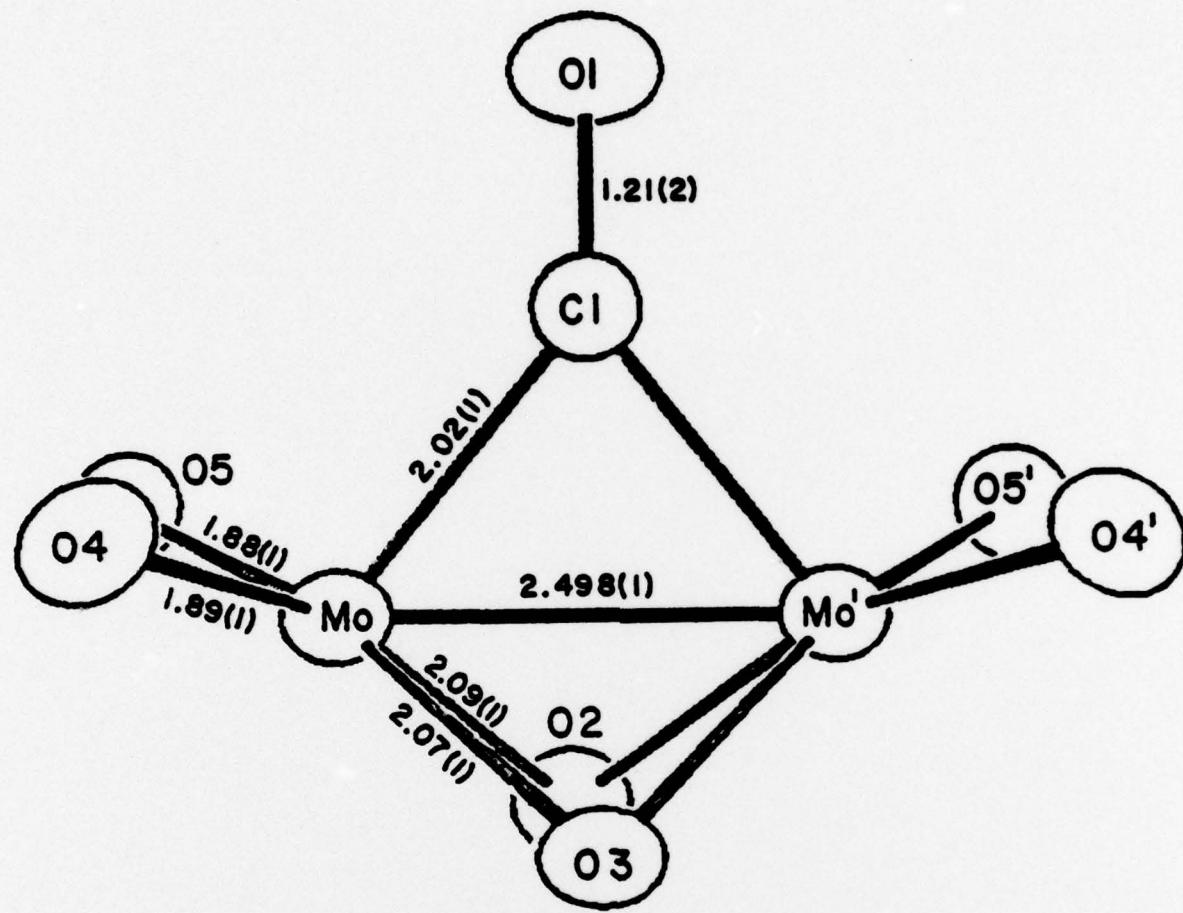
Fig. 1 A view of the coordination geometry of $\text{Mo}_2(\text{OBu}^t)_6\text{CO}$ showing the main internuclear distances. Each atom is represented by its thermal ellipsoid of vibration, scaled to enclose 40% of the electron density. The tertiary butyl groups are omitted for clarity.

Fig. 2 An ORTEP view of the $\text{Mo}_2(\text{OSi})_6(\text{NC}_2)_2$ portion of the $\text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$ molecule looking directly down the Mo-Mo bond with Mo(1) eclipsed by Mo(2). Atoms labelled in smaller print are bonded to Mo(1). All atoms are represented by 50% probability ellipsoids. Some important interatomic distances and angles are: Mo-Mo=2.242(1) \AA , Mo-O(av)=1.95 \AA , Mo-N_{av}=2.28 \AA , Mo-Mo-O(av)=102°, Mo-Mo-N(av)=95°.

Fig. 3 Schematic Representations for the molecular structures of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{un})$ compounds (a) un= $\text{RC}\equiv\text{CR}$ (b) un= $\text{CH}_2=\text{C}=\text{CH}_2$ and (c) un= Me_2NCN .

Fig. 4 Coordination Geometries of (A) $\text{Mo}_2(\text{OPr}^i)_8$ and (B) $\text{Mo}_2(\text{OPr}^i)_6(\text{NO})_2$ showing some pertinent bond distances. Distances shown for B are averaged over two independent molecules. In both A and B the molecules possess rigorous C_i and virtual C_{2h} symmetry.

Fig. 5 An ORTEP view of the $\text{W}_4(\text{OPr}^i)_{12}(\text{HOPr}^i)_2$ molecule showing only the W_4O_{14} skeleton. The molecule has C_i symmetry. Some important parameters are: W(1)-W(2)=2.46 \AA ; W(1)-W(1)'=3.30 \AA ; W(2)-W(1)-W(1)' angle 6=140°.



$\text{Mo}_2\text{O}_6(\text{CO})$ Skeleton of
 $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\text{CO})$

FIG.1

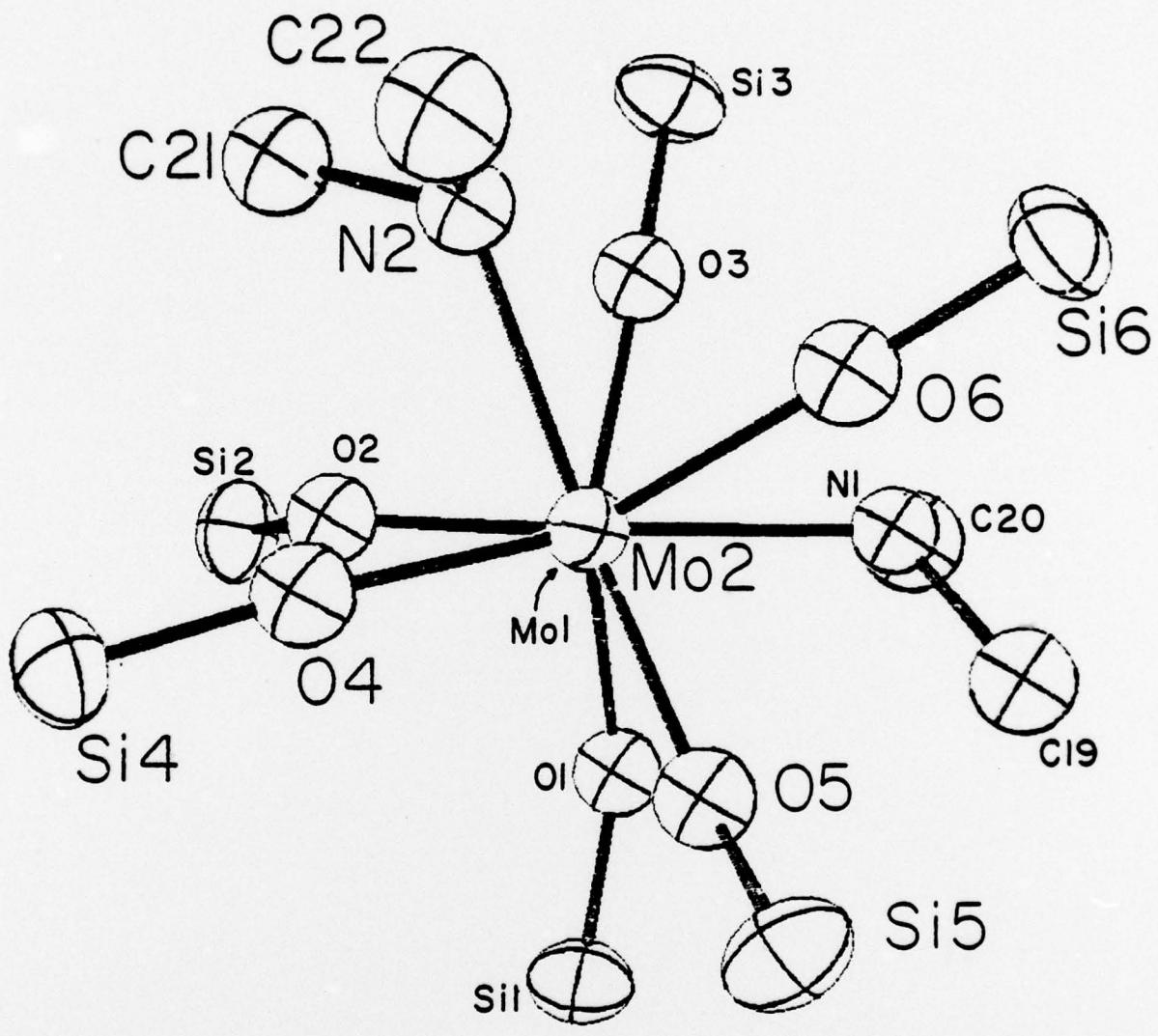
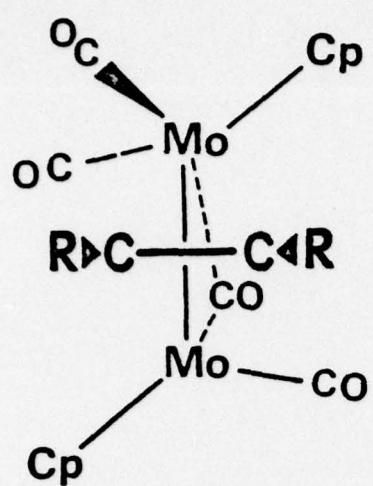
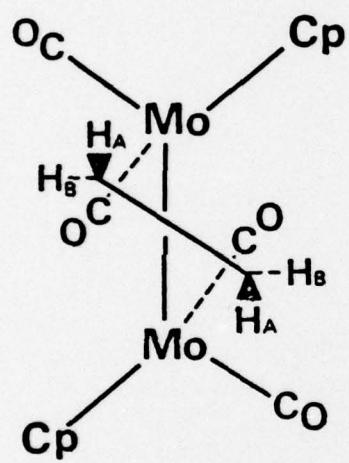


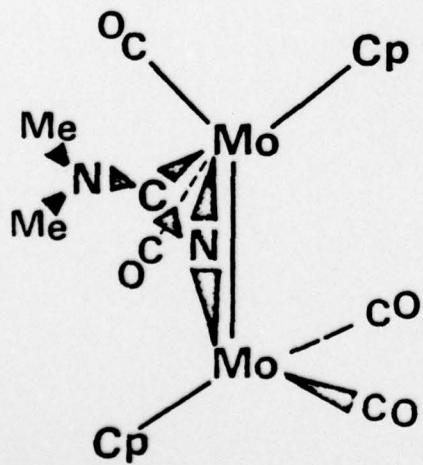
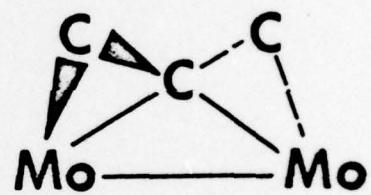
FIG. 2



(a)



(b)



(c)

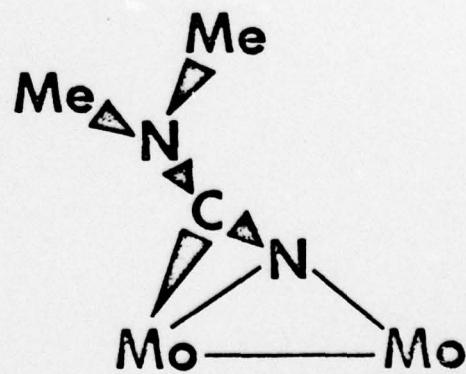


FIG. 3

$\text{Mo}_2(\text{O-i-Pr})_6(\text{NO})_2$
Skeleton



$\text{Mo}_2(\text{O-i-Pr})_8$
Skeleton

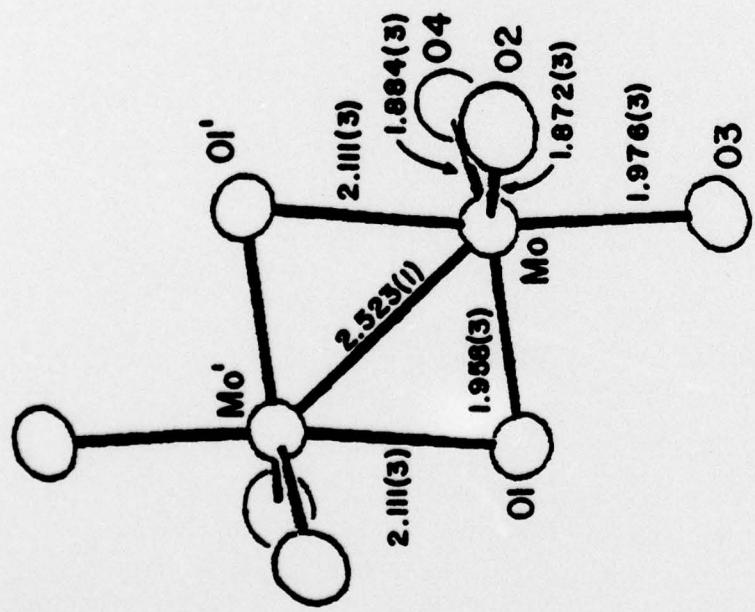
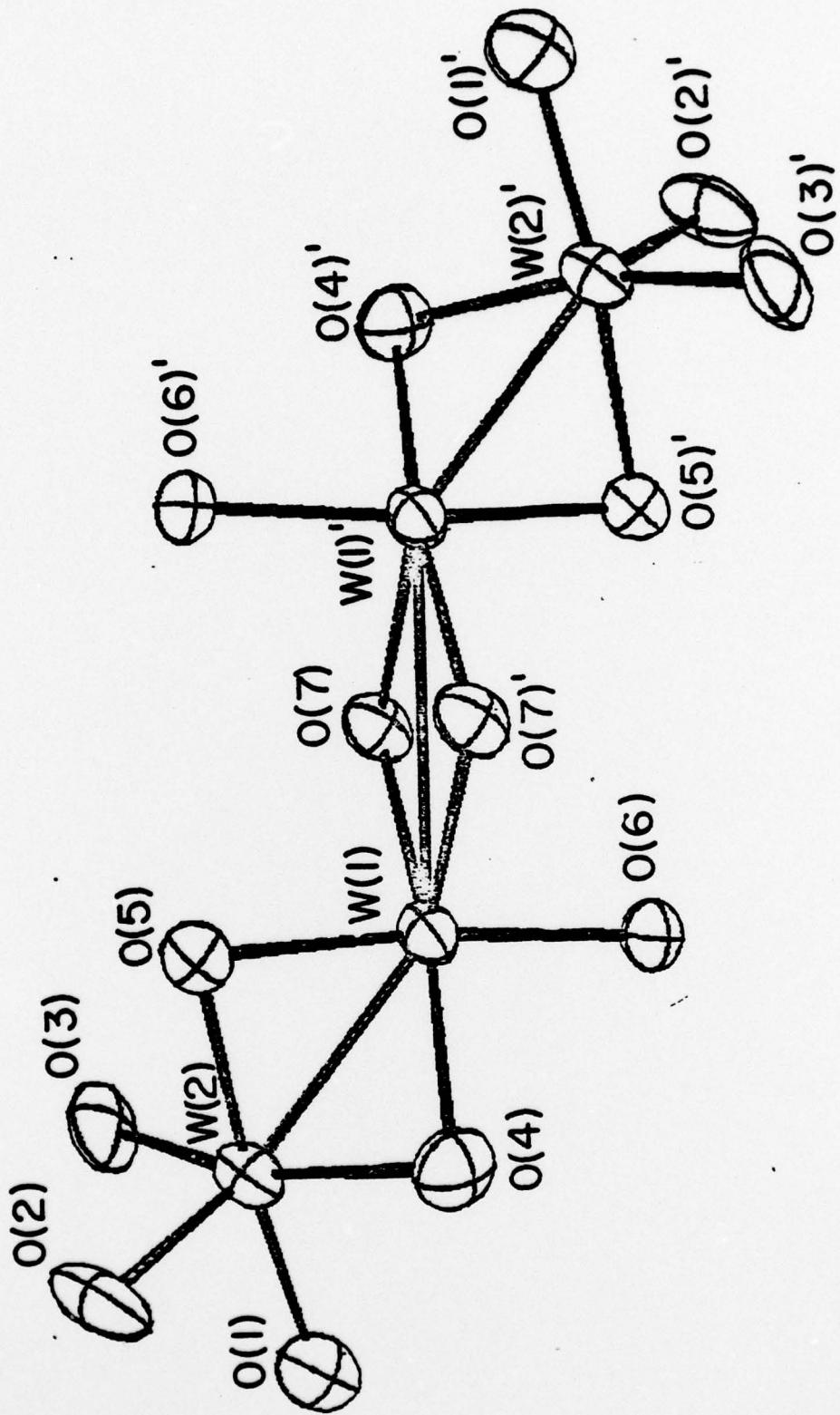


FIG. 5



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